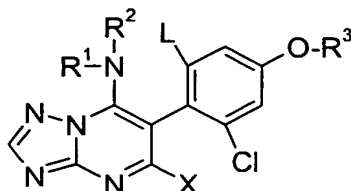


6-(2-Chloro-4-alkoxyphenyl)triazolopyrimidines, their preparation and their use for controlling harmful fungi, and compositions comprising these compounds

Description

5

The present invention relates to substituted triazolopyrimidines of the formula I



in which the substituents are as defined below:

10 L is hydrogen, chlorine or bromine;

R¹, R² independently of one another are hydrogen, C₁-C₈-alkyl, C₁-C₈-haloalkyl, C₃-C₈-cycloalkyl, C₃-C₈-halocycloalkyl, C₂-C₈-alkenyl, C₂-C₈-haloalkenyl, C₃-C₆-cycloalkenyl, C₃-C₆-halocycloalkenyl, C₂-C₈-alkynyl, C₂-C₈-haloalkynyl or phenyl, naphthyl or a five- or six-membered saturated, partially unsaturated or aromatic heterocycle which contains one to four heteroatoms from the group consisting of O, N and S,

20 R¹ and R² together with the nitrogen atom to which they are attached may also form a five- or six-membered heterocyclyl or heteroaryl which is attached via N and may contain one to three further heteroatoms from the group consisting of O, N and S as ring member and/or may carry one or more substituents from the group consisting of halogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₂-C₆-alkenyl, C₂-C₆-haloalkenyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₃-C₆-alkenyloxy, C₃-C₆-haloalkenyloxy, (exo)-C₁-C₆-alkylene and oxy-C₁-C₃-alkylenoxy;

R³ is C₁-C₈-alkyl, C₁-C₈-haloalkyl, C₃-C₈-alkenyl, C₃-C₈-haloalkenyl, C₃-C₈-alkynyl, C₃-C₈-haloalkynyl, C₃-C₈-cycloalkyl, C₃-C₈-halocycloalkyl, or phenyl-C₁-C₄-alkyl;

30 R¹, R² and/or R³ may carry one to four identical or different groups R^a:

35 R^a is halogen, cyano, nitro, hydroxyl, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₆-alkylcarbonyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkoxycarbonyl, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino, C₂-C₈-alkenyl, C₂-C₈-haloalkenyl, C₃-C₈-cycloalkenyl, C₂-C₆-alkenyloxy, C₃-C₆-haloalkenyloxy, C₂-C₆-alkynyl, C₂-C₆-haloalkynyl, C₃-C₆-alkynyloxy, C₃-C₆-haloalkynyloxy, C₃-C₆-cycloalkoxy, C₃-C₆-cycloalkenyloxy, oxy-C₁-C₃-

alkylenoxy, phenyl, naphthyl, a five- to ten-membered saturated, partially unsaturated or aromatic heterocycle which contains one to four heteroatoms from the group consisting of O, N and S,

5 where these aliphatic, alicyclic or aromatic groups for their part may be partially or fully halogenated or may carry one to three groups R^b:

10 R^b is halogen, cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocabonyl, alkyl, haloalkyl, alkenyl, alkenyloxy, alkynyloxy, alkoxy, haloalkoxy, alkylthio, alkylamino, dialkylamino, formyl, alkylcarbonyl, alkylsulfonyl, alkylsulfoxyl, alkoxy carbonyl, alkylcarbonyloxy, alkylaminocarbonyl, dialkylaminocarbonyl, alkylaminothiocarbonyl, dialkylaminothiocarbonyl, where the alkyl groups in these radicals
15 contain 1 to 6 carbon atoms and the abovementioned alkenyl or alkynyl groups in these radicals contain 2 to 8 carbon atoms;

and/or one to three of the following radicals:

20 cycloalkyl, cycloalkoxy, heterocyclyl, heterocyclyloxy, where the cyclic systems contain 3 to 10 ring members; aryl, aryloxy, arylthio, aryl-C₁-C₆-alkoxy, aryl-C₁-C₆-alkyl, hetaryl, hetaryloxy, het-arylthio, where the aryl radicals preferably contain 6 to 10 ring members and the hetaryl radicals 5 or 6 ring members, where the
25 cyclic systems may be partially or fully halogenated or substituted by alkyl or haloalkyl groups;

X is halogen, cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₂-haloalkoxy.

30 Moreover, the invention relates to processes and intermediates for preparing these compounds, to compositions comprising them and to their use for controlling phytopathogenic harmful fungi.

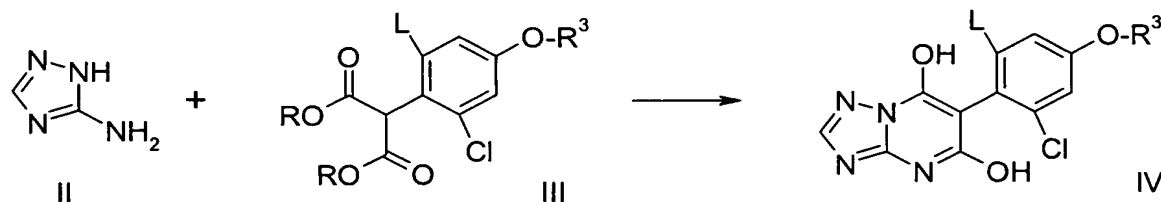
35 5-Chloro-6-phenyl-7-aminotriazolopyrimidines are known in a general manner from EP-A 71 792 and EP-A 550 113. 6-(2-Halo-4-alkoxyphenyl)triazolopyrimidines are proposed in a general manner in WO 99/48893. These compounds are known to be suitable for controlling harmful fungi.

The compounds according to the invention differ from those described in WO 99/48893 by the substitution in the ortho-positions of the 6-phenyl ring which, in the prior art, are substituted by at least one fluorine atom.

- 5 However, the activity of the known compounds is in many cases unsatisfactory. It is an object of the present invention to provide compounds having improved activity and/or a broader activity spectrum.

- 10 Accordingly, the compounds defined at the outset have been found. Moreover, processes and intermediates for their preparation, compositions comprising them and methods for controlling harmful fungi using the compounds I have been found.

- The compounds according to the invention can be obtained by different routes. Advantageously, they are prepared by reaction of 5-aminotriazole of the formula II with appropriately substituted phenyl malonates of the formula III in which R is alkyl, preferably C₁–C₆-alkyl, in particular methyl or ethyl.



- This reaction is usually carried out at temperatures of from 80°C to 250°C, preferably from 120°C to 180°C, without solvent or in an inert organic solvent in the presence of a base [cf. EP-A 770 615] or in the presence of acetic acid under the conditions known from Adv. Het. Chem. 57 (1993), 81 ff.

- Suitable solvents are aliphatic hydrocarbons, aromatic hydrocarbons, such as toluene, o-, m- and p-xylene, halogenated hydrocarbons, ethers, nitriles, ketones, alcohols, and also N-methylpyrrolidone, dimethyl sulfoxide, dimethylformamide and dimethylacetamide. With particular preference, the reaction is carried out in the absence of solvent or in chlorobenzene, xylene, dimethyl sulfoxide or N-methylpyrrolidone. It is also possible to use mixtures of the solvents mentioned.

- 30 Suitable bases are, in general, inorganic compounds, such as alkali metal and alkaline earth metal hydroxides, alkali metal and alkaline earth metal oxides, alkali metal and alkaline earth metal hydrides, alkali metal amides, alkali metal and alkaline earth metal carbonates, and also alkali metal bicarbonates, organometallic compounds, in particular alkali metal alkyls, alkyl magnesium halides and also alkali metal and alkaline earth metal alkoxides and dimethoxymagnesium, moreover organic bases, for example tertiary amines, such as trimethylamine, triethylamine, triisopropylethylamine,

tributylamine and N-methylpiperidine, N-methylmorpholine, pyridine, substituted pyridines, such as collidine, lutidine and 4-dimethylaminopyridine, and also bicyclic amines. Particular preference is given to using tertiary amines, such as triisopropylethylamine, tributylamine, N-methylmorpholine or N-methylpiperidine.

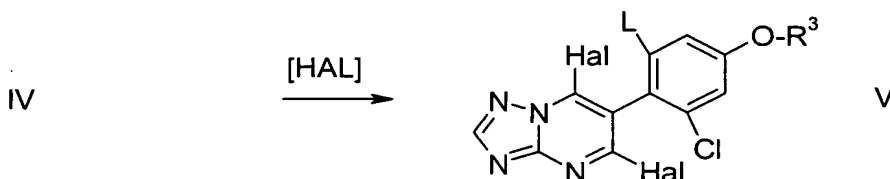
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The bases are generally employed in catalytic amounts; however, they can also be employed in equimolar amounts, in excess or, if appropriate, as solvent.

The starting materials are generally reacted with one another in equimolar amounts. In terms of yield, it may be advantageous to use an excess of the base and the malonate 10 III, based on the triazole.

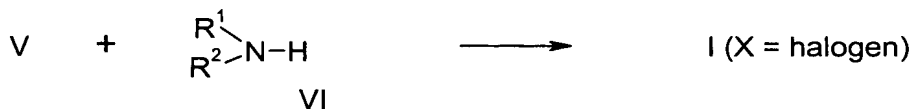
Phenylmalonates of the formula III are advantageously obtained from the reaction of appropriately substituted bromobenzenes with dialkyl malonates under Cu(I) catalysis 15 [cf. Chemistry Letters (1981), 367-370; EP-A 10 02 788].

The dihydroxytriazolopyrimidines of the formula IV are converted under the conditions known from WO-A 94/20501 into the dihalopyrimidines of the formula V in which Hal is a halogen atom, preferably a bromine or a chlorine atom, in particular a chlorine atom. 20 The halogenating agent [HAL] used is advantageously a chlorinating agent or a brominating agent, such as phosphorus oxybromide or phosphorus oxychloride, if appropriate in the presence of a solvent.



This reaction is usually carried out at from 0°C to 150°C, preferably from 80°C to 125°C 25 [cf. EP-A 770 615].

Dihalopyrimidines of the formula V are reacted further with amines of the formula VI



30 in which R¹ and R² are as defined in formula I, to give compounds of the formula I in which X is halogen.

This reaction is advantageously carried out at from 0°C to 70°C, preferably from 10°C to 35°C, preferably in the presence of an inert solvent, such as an ether, for example

dioxane, diethyl ether or, in particular, tetrahydrofuran, a halogenated hydrocarbon, such as dichloromethane, or an aromatic hydrocarbon, such as, for example, toluene [cf. WO-A 98/46608].

- 5 Preference is given to using a base, such as a tertiary amine, for example triethylamine, or an inorganic amine, such as potassium carbonate; it is also possible for excess amine of the formula VI to serve as base.

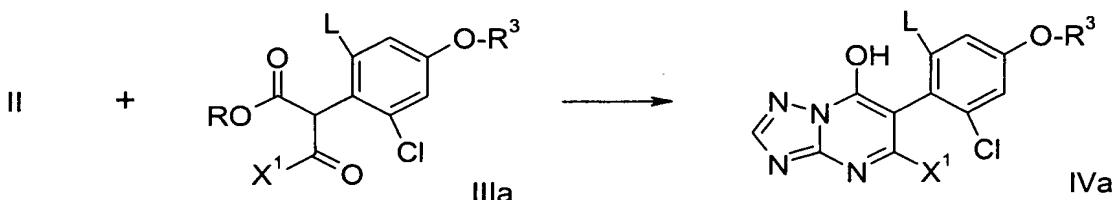
- 10 Compounds of the formula I in which X is cyano, C₁-C₆-alkoxy or C₁-C₂-haloalkoxy can be obtained in an advantageous manner by reacting compounds I in which X is halogen, preferably chlorine, with compounds M-X' (formula VII). Depending on the meaning of the group X' to be introduced, the compounds VII are inorganic cyanides, alkoxylates or haloalkoxylates. The reaction is advantageously carried out in the presence of an inert solvent. The cation M in formula VII is of little importance; for
15 for practical reasons, ammonium, tetraalkylammonium or alkali metal or alkaline earth metal salts are usually preferred.



The reaction temperature is usually from 0 to 120°C, preferably from 10 to 40°C [cf. J. Heterocycl. Chem. 12 (1975), 861-863].

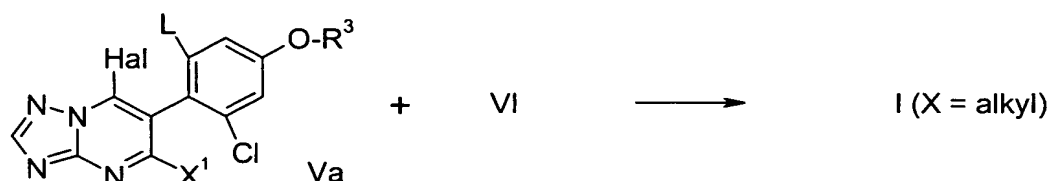
- 20 Suitable solvents include ethers, such as dioxane, diethyl ether and, preferably, tetrahydrofuran, halogenated hydrocarbons, such as dichloromethane, and aromatic hydrocarbons, such as toluene.

- 25 Compounds of the formula I, in which X is C₁-C₄-alkyl or C₁-C₄-haloalkyl can be obtained in an advantageous manner by the following synthesis route:



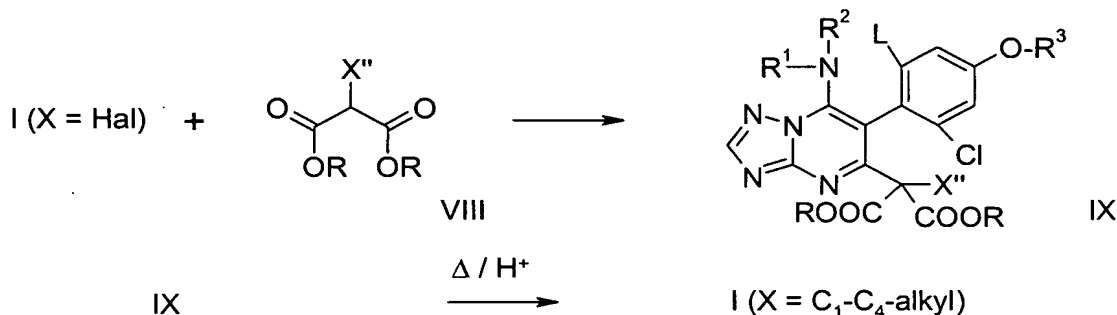
- Starting with the keto esters IIIa, 5-alkyl-7-hydroxy-6-phenyltriazolopyrimidines IVa are obtained. In the formulae IIIa and IVa, X¹ is C₁-C₄-alkyl or C₁-C₄-haloalkyl. By using
30 the easily obtainable 2-phenylacetoacetates (IIIa where X¹ = CH₃), the 5-methyl-7-hydroxy-6-phenyltriazolopyrimidines are obtained [cf. Chem. Pharm. Bull., 9 (1961), 801]. The starting materials IIIa are advantageously prepared under the conditions described in EP-A 10 02 788.

The resulting 5-alkyl-7-hydroxy-6-phenyltriazolopyrimidines are reacted with halogenating agents [HAL] under the conditions described further above to give the 7-halotriazolopyrimidines of the formula Va. Preference is given to using chlorinating or brominating agents such as phosphorus oxybromide, phosphorus oxychloride, thionyl chloride, thionyl bromide or sulfonyl chloride. The reaction can be carried out neat or in the presence of a solvent. Customary reaction temperatures are from 0 to 150°C or, preferably, from 80 to 125°C.



The reaction of Va with amines VI is carried out under the conditions described further above.

Alternatively, compounds of the formula I in which X is C₁-C₄-alkyl can also be prepared from compounds I in which X is halogen, in particular chlorine, and malonates of the formula VIII. In formula VIII, X'' is hydrogen or C₁-C₃-alkyl and R is C₁-C₄-alkyl. They are reacted to give compounds of the formula IX and decarboxylated to give compounds I [cf. US 5,994,360].



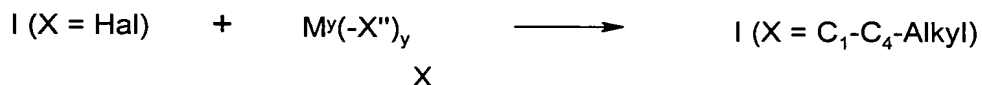
The malonates VIII are known from the literature [J. Am. Chem. Soc., 64 (1942), 2714; J. Org. Chem., 39 (1974), 2172; Helv. Chim. Acta, 61 (1978), 1565], or they can be prepared in accordance with the literature cited.

The subsequent hydrolysis of the ester IX is carried out under generally customary conditions; depending on the various structural elements, alkaline or acidic hydrolysis of the compounds IX may be advantageous. Under the conditions of the ester hydrolysis, there may be complete or partial decarboxylation to I.

The decarboxylation is usually carried out at temperatures of from 20°C to 180°C, preferably from 50°C to 120°C, in an inert solvent, if appropriate in the presence of an acid.

- 5 Suitable acids are hydrochloric acid, sulfuric acid, phosphoric acid, formic acid, acetic acid, p-toluenesulfonic acid. Suitable solvents are water, aliphatic hydrocarbons, such as pentane, hexane, cyclohexane and petroleum ether, aromatic hydrocarbons, such as toluene, o-, m- and p-xylene, halogenated hydrocarbons, such as methylene chloride, chloroform and chlorobenzene, ethers, such as diethyl ether, diisopropyl
 10 ether, tert-butyl methyl ether, dioxane, anisole and tetrahydrofuran, nitriles, such as acetonitrile and propionitrile, ketones, such as acetone, methyl ethyl ketone, diethyl ketone and tert-butyl methyl ketone, alcohols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol and tert-butanol, and also dimethyl sulfoxide, dimethylformamide and dimethyl acetamide; particularly preferably, the reaction is
 15 carried out in hydrochloric acid or acetic acid. It is also possible to use mixtures of the solvents mentioned.

- Compounds of the formula I in which X is C₁-C₄-alkyl can also be obtained by coupling
 5-halotriazolopyrimidines of the formula I in which X is halogen with organometallic
 20 reagents of the formula X. In one embodiment of this process, the reaction is carried out with transition metal catalysis, such as Ni or Pd catalysis.



- In formula X, M is a metal ion of the valency y, such as, for example, B, Zn or Sn, and
 X'' is C₁-C₃-alkyl. This reaction can be carried out, for example, analogously to the
 25 following methods: J. Chem. Soc. Perkin Trans. 1, (1994), 1187, *ibid* 1 (1996), 2345; WO-A 99/41255; Aust. J. Chem. 43 (1990), 733; J. Org. Chem. 43 (1978), 358; J. Chem. Soc. Chem. Commun. (1979), 866; Tetrahedron Lett. 34 (1993), 8267; *ibid* 33 (1992), 413.

- 30 The reaction mixtures are worked up in a customary manner, for example by mixing with water, separating the phases and, if appropriate, chromatographic purification of the crude products. Some of the intermediates and end products are obtained in the form of colorless or slightly brownish viscous oils which are purified or freed from volatile components under reduced pressure and at moderately elevated temperature.
 35 If the intermediates and end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

If individual compounds I cannot be obtained by the routes described above, they can be prepared by derivatization of other compounds I.

5 If the synthesis yields mixtures of isomers, a separation is generally not necessarily required however since in some cases the individual isomers can be interconverted during work-up for use or during use (for example under the action of light, acids or bases). Such conversions may also take place after use, for example in the treatment of plants in the treated plant, or in the harmful fungus to be controlled.

10 In the definitions of the symbols given in the formulae above, collective terms were used which are generally representative of the following substituents:

halogen: fluorine, chlorine, bromine and iodine;

15 alkyl: saturated straight-chain or branched hydrocarbon radicals having 1 to 4, 6 or 8 carbon atoms, for example C₁-C₆-alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl,
20 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;

haloalkyl: straight-chain or branched alkyl groups having 1 to 2, 4 or 6 carbon atoms
25 (as mentioned above), where in these groups some or all of the hydrogen atoms may be replaced by halogen atoms as mentioned above: in particular, C₁-C₂-haloalkyl, such as chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2-fluoroethyl,
30 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl or 1,1,1-trifluoroprop-2-yl;

alkenyl: unsaturated straight-chain or branched hydrocarbon radicals having 2 to 4, 6
35 or 8 carbon atoms and one or two double bonds in any position, for example C₂-C₆-alkenyl, such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-
40 butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-

- propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl, 2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl-2-methyl-1-propenyl and 1-ethyl-2-methyl-2-propenyl;
- 15 haloalkenyl: unsaturated straight-chain or branched hydrocarbon radicals having 2 to 8 carbon atoms and one or two double bonds in any position (as mentioned above), where in these groups some or all of the hydrogen atoms may be replaced by halogen atoms as mentioned above, in particular by fluorine, chlorine and bromine;
- 20 alkynyl: straight-chain or branched hydrocarbon groups having 2 to 4, 6 or 8 carbon atoms and one or two triple bonds in any position, for example C₂-C₈-alkynyl, such as ethynyl, 1-propynyl, 2-propynyl, 1-butyne, 2-butyne, 3-butyne, 1-methyl-2-propynyl, 1-pentyne, 2-pentyne, 3-pentyne, 4-pentyne, 1-methyl-2-butyne, 1-methyl-3-butyne, 2-methyl-3-butyne, 3-methyl-1-butyne, 1,1-dimethyl-2-propynyl, 1-ethyl-2-propynyl,
- 25 1-hexynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 1-methyl-2-pentyne, 1-methyl-3-pentyne, 1-methyl-4-pentyne, 2-methyl-3-pentyne, 2-methyl-4-pentyne, 3-methyl-1-pentyne, 3-methyl-4-pentyne, 4-methyl-1-pentyne, 4-methyl-2-pentyne, 1,1-dimethyl-2-butyne, 1,1-dimethyl-3-butyne, 1,2-dimethyl-3-butyne, 2,2-dimethyl-3-butyne, 3,3-dimethyl-1-butyne, 1-ethyl-2-butyne, 1-ethyl-3-butyne, 2-ethyl-3-butyne and 1-ethyl-1-methyl-2-propynyl;
- 30 cycloalkyl: mono- or bicyclic saturated hydrocarbon groups having 3 to 6 or 8 carbon ring members, for example C₃-C₈-cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl;
- 35 five- to ten-membered saturated, partially unsaturated or aromatic heterocycle which contains one to four heteroatoms from the group consisting of O, N and S:
- 40 - 5- or 6-membered heterocyclyl which contains one to three nitrogen atoms and/or one oxygen or sulfur atom or one or two oxygen and/or sulfur atoms, for example 2-

tetrahydrofuranyl, 3-tetrahydrofuranyl, 2-tetrahydrothienyl, 3-tetrahydrothienyl, 2-pyrrolidinyl, 3-pyrrolidinyl, 3-isoxazolidinyl, 4-isoxazolidinyl, 5-isoxazolidinyl, 3-isothiazolidinyl, 4-isothiazolidinyl, 5-isothiazolidinyl, 3-pyrazolidinyl, 4-pyrazolidinyl, 5-pyrazolidinyl, 2-oxazolidinyl, 4-oxazolidinyl, 5-oxazolidinyl, 2-thiazolidinyl, 4-thiazolidinyl, 5-thiazolidinyl, 2-imidazolidinyl, 4-imidazolidinyl, 2-pyrrolin-2-yl, 2-pyrrolin-3-yl, 3-pyrrolin-2-yl, 3-pyrrolin-3-yl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1,3-dioxan-5-yl, 2-tetrahydropyranyl, 4-tetrahydropyranyl, 2-tetrahydrothienyl, 3-hexahydropyridazinyl, 4-hexahydropyridazinyl, 2-hexahydropyrimidinyl, 4-hexahydropyrimidinyl, 5-hexahydropyrimidinyl and 2-piperazinyl;

10

- 5-membered heteroaryl which contains one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom: 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl and 1,3,4-triazol-2-yl;

15

- 6-membered heteroaryl which contains one to three or one to four nitrogen atoms: 6-membered heteroaryl groups which, in addition to carbon atoms, may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl and 2-pyrazinyl;

20

25 alkylene: divalent unbranched chains of 3 to 5 CH₂ groups, for example CH₂, CH₂CH₂, CH₂CH₂CH₂, CH₂CH₂CH₂CH₂ and CH₂CH₂CH₂CH₂CH₂;

25

oxyalkylene: divalent unbranched chains of 2 to 4 CH₂ groups, where one valency is attached to the skeleton via an oxygen atom, for example OCH₂CH₂, OCH₂CH₂CH₂ and OCH₂CH₂CH₂CH₂;

30

oxyalkylenoxy: divalent unbranched chains of 1 to 3 CH₂ groups, where both valencies are attached to the skeleton via an oxygen atom, for example OCH₂O, OCH₂CH₂O and OCH₂CH₂CH₂O.

35

The scope of the present invention includes the (R)- and (S)-isomers and the racemates of compounds of the formula I having chiral centers.

40

The particularly preferred embodiments of the intermediates with respect to the variables correspond to those of radicals L and R³ of formula I.

With a view to the intended use of the triazolopyrimidines of the formula I, particular preference is given to the following meanings of the substituents, in each case on their own or in combination:

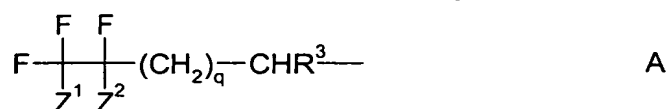
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Preference is given to compounds of the formula I in which R¹ is not hydrogen.

Particular preference is given to compounds I in which R¹ is C₁-C₆-alkyl, C₂-C₆-alkenyl or C₁-C₈-haloalkyl.

10

Preference is given to compounds I in which R¹ is a group A:



in which

15 Z¹ is hydrogen, fluorine or C₁-C₆-fluoroalkyl,

Z² is hydrogen or fluorine, or

Z¹ and Z² together form a double bond;

q is 0 or 1; and

R³ is hydrogen or methyl.

20

Moreover, preference is given to compounds I in which R¹ is C₃-C₆-cycloalkyl which may be substituted by C₁-C₄-alkyl.

Particular preference is given to compounds I in which R² is hydrogen.

25

Preference is likewise given to compounds I in which R² is methyl or ethyl.

If R¹ and/or R² comprise haloalkyl or haloalkenyl groups having a center of chirality, the (S) isomers are preferred for these groups. In the case of halogen-free alkyl or alkenyl groups having a center of chirality in R¹ or R², preference is given to the (R) configured isomers.

30

Preference is furthermore given to compounds I in which R¹ and R² together with the nitrogen atom to which they are attached form a piperidinyl, morpholinyl or thiomorpholinyl ring, in particular a piperidinyl ring, which, if appropriate, is substituted by one to three groups halogen, C₁-C₄-alkyl or C₁-C₄-haloalkyl. Particular preference is given to the compounds in which R¹ and R² together with the nitrogen atom to which they are attached form a 4-methylpiperidine ring.

35

The invention furthermore preferably provides compounds I in which R¹ and R² together with the nitrogen atom to which they are attached form a pyrazole ring which, if appropriate, is substituted by one or two groups halogen, C₁-C₄-alkyl or C₁-C₄-haloalkyl, in particular by 3,5-dimethyl or 3,5-di(trifluoromethyl).

5

In addition, particular preference is also given to compounds of the formula I in which R¹ is CH(CH₃)-CH₂CH₃, CH(CH₃)-CH(CH₃)₂, CH(CH₃)-C(CH₃)₃, CH(CH₃)-CF₃, CH₂C(CH₃)=CH₂, CH₂CH=CH₂, cyclopentyl or cyclohexyl; R² is hydrogen or methyl; or R¹ and R² together are -(CH₂)₂CH(CH₃)(CH₂)₂-, -(CH₂)₂CH(CF₃)(CH₂)₂-

10 or -(CH₂)₂O(CH₂)₂-.

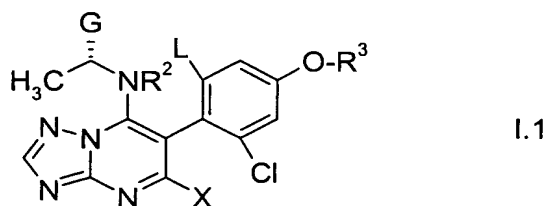
Preference is given to compounds I in which the group L is hydrogen or chlorine, in particular chlorine.

15 In addition, preference is also given to compounds I in which R³ is C₁-C₄-alkyl, halomethyl or allyl, in particular methyl.

Preference is given to compounds I in which X is halogen, C₁-C₄-alkyl, cyano or C₁-C₄-alkoxy, such as chlorine, methyl, cyano, methoxy or ethoxy, especially chlorine or methyl, in particular chlorine.

20

A preferred embodiment of the invention relates to compounds of the formula I.1:



in which

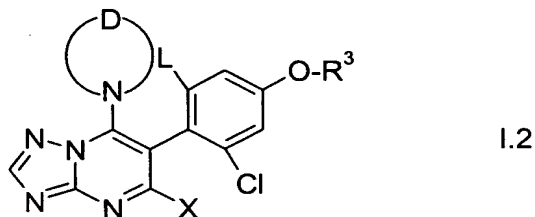
25 G is C₂-C₆-alkyl, in particular ethyl, n- and isopropyl, n-, sec-, tert-butyl, and C₁-C₄-alkoxymethyl, in particular ethoxymethyl, or C₃-C₆-cycloalkyl, in particular cyclopentyl or cyclohexyl;
 R² is hydrogen or methyl; and
 X is chlorine, methyl, cyano, methoxy or ethoxy.

30

A further preferred embodiment of the invention relates to compounds in which R¹ and R² together with the nitrogen atom to which they are attached form a five- or six-membered heterocyclyl or heteroaryl which is attached via N and may contain a further heteroatom from the group consisting of O, N and S as ring member and/or may carry one or more substituents from the group consisting of halogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₂-C₆-alkenyl, C₂-C₆-haloalkenyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy,

35

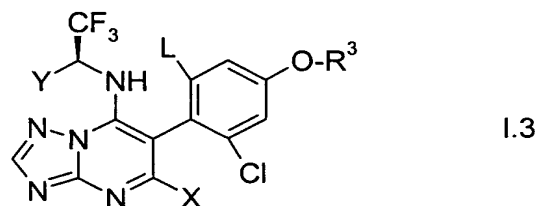
C₃-C₆-alkenyloxy, C₃-C₆-haloalkenyloxy, C₁-C₆-alkylene and oxy-C₁-C₃-alkylenoxy. These compounds correspond in particular to formula I.2,



in which

- 5 D together with the nitrogen atom forms a five- or six-membered heterocyclyl or heteroaryl which is attached via N and may contain a further heteroatom from the group consisting of O, N and S as ring member and/or may carry one or more substituents from the group consisting of halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy and C₁-C₂-haloalkyl; and
- 10 X is chlorine, methyl, cyano, methoxy or ethoxy.

A further preferred embodiment of the invention relates to compounds of the formula I.3



- 15 in which Y is hydrogen or C₁-C₄-alkyl, in particular methyl and ethyl, and X is chlorine, methyl, cyano, methoxy or ethoxy.

In particular with a view to their use, preference is given to the compounds I compiled in the tables below. Moreover, the groups mentioned for a substituent in the tables are per se, independently of the combination in which they are mentioned, a particularly

20 preferred embodiment of the substituent in question.

Table 1

Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is methyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

25

Table 2

Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is ethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 3

Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is n-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

5 Table 4

Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is tert-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 5

- 10 Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is fluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 6

- 15 Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is difluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 7

- 20 Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is trifluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 8

- 25 Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is 2-fluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 9

- 30 Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is 2,2-difluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 10

- 35 Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is 2,2,2-trifluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 11

Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is benzyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

5 Table 12

Compounds of the formula I in which X is chlorine, L is hydrogen, R³ is allyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 13

- 10 Compounds of the formula I in which X and L are chlorine, R³ is methyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 14

- 15 Compounds of the formula I in which X and L are chlorine, R³ is ethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 15

- 20 Compounds of the formula I in which X and L are chlorine, R³ is n-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 16

- Compounds of the formula I in which X and L are chlorine, R³ is tert-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

25 Table 17

Compounds of the formula I in which X and L are chlorine, R³ is fluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 18

- 30 Compounds of the formula I in which X and L are chlorine, R³ is difluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 19

- 35 Compounds of the formula I in which X and L are chlorine, R³ is trifluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 20

- 40 Compounds of the formula I in which X and L are chlorine, R³ is 2-fluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 21

Compounds of the formula I in which X and L are chlorine, R³ is 2,2-difluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

5 Table 22

Compounds of the formula I in which X and L are chlorine, R³ is 2,2,2-trifluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 23

- 10 Compounds of the formula I in which X and L are chlorine, R³ is benzyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 24

- 15 Compounds of the formula I in which X and L are chlorine, R³ is allyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 25

- 20 Compounds of the formula I in which X is methyl, L is hydrogen, R³ is methyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 26

Compounds of the formula I in which X is methyl, L is hydrogen, R³ is ethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

25 Table 27

Compounds of the formula I in which X is methyl, L is hydrogen, R³ is n-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 28

- 30 Compounds of the formula I in which X is methyl, L is hydrogen, R³ is tert-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 29

- 35 Compounds of the formula I in which X is methyl, L is hydrogen, R³ is fluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 30

- 40 Compounds of the formula I in which X is methyl, L is hydrogen, R³ is difluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 31

Compounds of the formula I in which X is methyl, L is hydrogen, R³ is trifluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of

5 table A.

Table 32

Compounds of the formula I in which X is methyl, L is hydrogen, R³ is 2-fluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

10

Table 33

Compounds of the formula I in which X is methyl, L is hydrogen, R³ is 2,2-difluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

15

Table 34

Compounds of the formula I in which X is methyl, L is hydrogen, R³ is 2,2,2-trifluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

20

Table 35

Compounds of the formula I in which X is methyl, L is hydrogen, R³ is benzyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

25

Table 36

Compounds of the formula I in which X is methyl, L is hydrogen, R³ is allyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 37

Compounds of the formula I in which X is methyl, L is chlorine, R³ is methyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

30

Table 38

Compounds of the formula I in which X is methyl, L is chlorine, R³ is ethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

35

Table 39

Compounds of the formula I in which X is methyl, L is chlorine, R³ is n-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

40

Table 40

Compounds of the formula I in which X is methyl, L is chlorine, R³ is tert-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

5 Table 41

Compounds of the formula I in which X is methyl, L is chlorine, R³ is fluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 42

- 10 Compounds of the formula I in which X is methyl, L is chlorine, R³ is difluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 43

- 15 Compounds of the formula I in which X is methyl, L is chlorine, R³ is trifluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 44

- 20 Compounds of the formula I in which X is methyl, L is chlorine, R³ is 2-fluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 45

- 25 Compounds of the formula I in which X is methyl, L is chlorine, R³ is 2,2-difluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 46

- 30 Compounds of the formula I in which X is methyl, L is chlorine, R³ is 2,2,2-trifluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 47

- Compounds of the formula I in which X is methyl, L is chlorine, R³ is benzyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

35 Table 48

Compounds of the formula I in which X is methyl, L is chlorine, R³ is allyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 49

Compounds of the formula I in which X is cyano, L is hydrogen, R³ is methyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

5 Table 50

Compounds of the formula I in which X is cyano, L is hydrogen, R³ is ethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 51

- 10 Compounds of the formula I in which X is cyano, L is hydrogen, R³ is n-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 52

- 15 Compounds of the formula I in which X is cyano, L is hydrogen, R³ is tert-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 53

- 20 Compounds of the formula I in which X is cyano, L is hydrogen, R³ is fluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 54

- 25 Compounds of the formula I in which X is cyano, L is hydrogen, R³ is difluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 55

- 30 Compounds of the formula I in which X is cyano, L is hydrogen, R³ is trifluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 56

- Compounds of the formula I in which X is cyano, L is hydrogen, R³ is 2-fluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

35 Table 57

Compounds of the formula I in which X is cyano, L is hydrogen, R³ is 2,2-difluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 58

Compounds of the formula I in which X is cyano, L is hydrogen, R³ is 2,2,2-trifluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

5

Table 59

Compounds of the formula I in which X is cyano, L is hydrogen, R³ is benzyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

10 Table 60

Compounds of the formula I in which X is cyano, L is hydrogen, R³ is allyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 61

15 Compounds of the formula I in which X is cyano, L is chlorine, R³ is methyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 62

20 Compounds of the formula I in which X is cyano, L is chlorine, R³ is ethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 63

25 Compounds of the formula I in which X is cyano, L is chlorine, R³ is n-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 64

Compounds of the formula I in which X is cyano, L is chlorine, R³ is tert-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

30 Table 65

Compounds of the formula I in which X is cyano, L is chlorine, R³ is fluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 66

35 Compounds of the formula I in which X is cyano, L is chlorine, R³ is difluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 67

40 Compounds of the formula I in which X is cyano, L is chlorine, R³ is trifluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 68

Compounds of the formula I in which X is cyano, L is chlorine, R³ is 2-fluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

5

Table 69

Compounds of the formula I in which X is cyano, L is chlorine, R³ is 2,2-difluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

10

Table 70

Compounds of the formula I in which X is cyano, L is chlorine, R³ is 2,2,2-trifluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

15

Table 71

Compounds of the formula I in which X is cyano, L is chlorine, R³ is benzyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

20

Table 72

Compounds of the formula I in which X is cyano, L is chlorine, R³ is allyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 73

25

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is methyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 74

30

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is ethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 75

35

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is n-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 76

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is tert-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 77

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is fluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

5

Table 78

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is difluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

10

Table 79

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is trifluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

15

Table 80

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is 2-fluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

20

Table 81

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is 2,2-difluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

25

Table 82

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is 2,2,2-trifluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

30

Table 83

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is benzyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

35

Table 84

Compounds of the formula I in which X is methoxy, L is hydrogen, R³ is allyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 85

Compounds of the formula I in which X is methoxy, L is chlorine, R³ is methyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

5 Table 86

Compounds of the formula I in which X is methoxy, L is chlorine, R³ is ethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 87

- 10 Compounds of the formula I in which X is methoxy, L is chlorine, R³ is n-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 88

- 15 Compounds of the formula I in which X is methoxy, L is chlorine, R³ is tert-butyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 89

- 20 Compounds of the formula I in which X is methoxy, L is chlorine, R³ is fluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 90

- 25 Compounds of the formula I in which X is methoxy, L is chlorine, R³ is difluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 91

- 30 Compounds of the formula I in which X is methoxy, L is chlorine, R³ is trifluoromethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 92

- 35 Compounds of the formula I in which X is methoxy, L is chlorine, R³ is 2-fluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 93

Compounds of the formula I in which X is methoxy, L is chlorine, R³ is 2,2-difluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 94

Compounds of the formula I in which X is methoxy, L is chlorine, R³ is 2,2,2-trifluoroethyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

5

Table 95

Compounds of the formula I in which X is methoxy, L is chlorine, R³ is benzyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

10 Table 96

Compounds of the formula I in which X is methoxy, L is chlorine, R³ is allyl and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 97

15 Compounds of the formula I in which L is hydrogen, R³ is n-propyl and X is cyano and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 98

20 Compounds of the formula I in which L is chlorine, R³ is n-propyl and X is cyano and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 99

25 Compounds of the formula I in which L is hydrogen, R³ is isopropyl and X is cyano and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 100

Compounds of the formula I in which L is chlorine, R³ is isopropyl and X is cyano and the combination of R¹ and R² corresponds for each compound to one row of table A.

30 Table 101

Compounds of the formula I in which L is hydrogen, R³ is 2-methoxyethyl and X is cyano and the combination of R¹ and R² corresponds for each compound to one row of table A.

35 Table 102

Compounds of the formula I in which L is chlorine, R³ is 2-methoxyethyl and X is cyano and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 103

Compounds of the formula I in which L is hydrogen, R³ is n-propyl and X is methoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

5

Table 104

Compounds of the formula I in which L is chlorine, R³ is n-propyl and X is methoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

10 Table 105

Compounds of the formula I in which L is hydrogen, R³ is isopropyl and X is methoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

15 Table 106

Compounds of the formula I in which L is chlorine, R³ is isopropyl and X is methoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 107

20 Compounds of the formula I in which L is hydrogen, R³ is 2-methoxyethyl and X is methoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 108

25 Compounds of the formula I in which L is chlorine, R³ is 2-methoxyethyl and X is methoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 109

30 Compounds of the formula I in which L is hydrogen, R³ is methyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 110

35 Compounds of the formula I in which L is chlorine, R³ is methyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 111

40 Compounds of the formula I in which L is hydrogen, R³ is ethyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 112

Compounds of the formula I in which L is chlorine, R³ is ethyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

5 Table 113

Compounds of the formula I in which L is hydrogen, R³ is n-propyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 114

10 Compounds of the formula I in which L is chlorine, R³ is n-propyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 115

15 Compounds of the formula I in which L is hydrogen, R³ is isopropyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 116

20 Compounds of the formula I in which L is chlorine, R³ is isopropyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 117

25 Compounds of the formula I in which L is hydrogen, R³ is 2-fluoroethyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 118

30 Compounds of the formula I in which L is chlorine, R³ is 2-fluoroethyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 119

Compounds of the formula I in which L is hydrogen, R³ is allyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

35 Table 120

Compounds of the formula I in which L is chlorine, R³ is allyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

Table 121

Compounds of the formula I in which L is hydrogen, R³ is 2-methoxyethyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

5

Table 122

Compounds of the formula I in which L is chlorine, R³ is 2-methoxyethyl and X is ethoxy and the combination of R¹ and R² corresponds for each compound to one row of table A.

10

Table A

No.	R ¹	R ²
A-1	H	H
A-2	CH ₃	H
A-3	CH ₃	CH ₃
A-4	CH ₂ CH ₃	H
A-5	CH ₂ CH ₃	CH ₃
A-6	CH ₂ CH ₃	CH ₂ CH ₃
A-7	CH ₂ CF ₃	H
A-8	CH ₂ CF ₃	CH ₃
A-9	CH ₂ CF ₃	CH ₂ CH ₃
A-10	CH ₂ CCl ₃	H
A-11	CH ₂ CCl ₃	CH ₃
A-12	CH ₂ CCl ₃	CH ₂ CH ₃
A-13	CH ₂ CH ₂ CH ₃	H
A-14	CH ₂ CH ₂ CH ₃	CH ₃
A-15	CH ₂ CH ₂ CH ₃	CH ₂ CH ₃
A-16	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃
A-17	CH(CH ₃) ₂	H
A-18	CH(CH ₃) ₂	CH ₃
A-19	CH(CH ₃) ₂	CH ₂ CH ₃
A-20	CH ₂ CH ₂ CH ₂ CH ₃	H
A-21	CH ₂ CH ₂ CH ₂ CH ₃	CH ₃
A-22	CH ₂ CH ₂ CH ₂ CH ₃	CH ₂ CH ₃
A-23	CH ₂ CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃
A-24	CH ₂ CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₂ CH ₃
A-25	(±) CH(CH ₃)-CH ₂ CH ₃	H

No.	R ¹	R ²
A-26	(±) CH(CH ₃)-CH ₂ CH ₃	CH ₃
A-27	(±) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
A-28	(S) CH(CH ₃)-CH ₂ CH ₃	H
A-29	(S) CH(CH ₃)-CH ₂ CH ₃	CH ₃
A-30	(S) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
A-31	(R) CH(CH ₃)-CH ₂ CH ₃	H
A-32	(R) CH(CH ₃)-CH ₂ CH ₃	CH ₃
A-33	(R) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
A-34	(±) CH(CH ₃)-CH(CH ₃) ₂	H
A-35	(±) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
A-36	(±) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
A-37	(S) CH(CH ₃)-CH(CH ₃) ₂	H
A-38	(S) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
A-39	(S) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
A-40	(R) CH(CH ₃)-CH(CH ₃) ₂	H
A-41	(R) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
A-42	(R) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
A-43	(±) CH(CH ₃)-C(CH ₃) ₃	H
A-44	(±) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-45	(±) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-46	(S) CH(CH ₃)-C(CH ₃) ₃	H
A-47	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-48	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-49	(R) CH(CH ₃)-C(CH ₃) ₃	H
A-50	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-51	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-52	(±) CH(CH ₃)-CF ₃	H
A-53	(±) CH(CH ₃)-CF ₃	CH ₃
A-54	(±) CH(CH ₃)-CF ₃	CH ₂ CH ₃
A-55	(S) CH(CH ₃)-CF ₃	H
A-56	(S) CH(CH ₃)-CF ₃	CH ₃
A-57	(S) CH(CH ₃)-CF ₃	CH ₂ CH ₃
A-58	(R) CH(CH ₃)-CF ₃	H
A-59	(R) CH(CH ₃)-CF ₃	CH ₃
A-60	(R) CH(CH ₃)-CF ₃	CH ₂ CH ₃
A-61	(±) CH(CH ₃)-CCl ₃	H
A-62	(±) CH(CH ₃)-CCl ₃	CH ₃

No.	R ¹	R ²
A-63	(±) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
A-64	(S) CH(CH ₃)-CCl ₃	H
A-65	(S) CH(CH ₃)-CCl ₃	CH ₃
A-66	(S) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
A-67	(R) CH(CH ₃)-CCl ₃	H
A-68	(R) CH(CH ₃)-CCl ₃	CH ₃
A-69	(R) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
A-70	CH ₂ CF ₂ CF ₃	H
A-71	CH ₂ CF ₂ CF ₃	CH ₃
A-72	CH ₂ CF ₂ CF ₃	CH ₂ CH ₃
A-73	CH ₂ (CF ₂) ₂ CF ₃	H
A-74	CH ₂ (CF ₂) ₂ CF ₃	CH ₃
A-75	CH ₂ (CF ₂) ₂ CF ₃	CH ₂ CH ₃
A-76	CH ₂ C(CH ₃)=CH ₂	H
A-77	CH ₂ C(CH ₃)=CH ₂	CH ₃
A-78	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃
A-79	CH ₂ CH=CH ₂	H
A-80	CH ₂ CH=CH ₂	CH ₃
A-81	CH ₂ CH=CH ₂	CH ₂ CH ₃
A-82	CH(CH ₃)CH=CH ₂	H
A-83	CH(CH ₃)CH=CH ₂	CH ₃
A-84	CH(CH ₃)CH=CH ₂	CH ₂ CH ₃
A-85	CH(CH ₃)C(CH ₃)=CH ₂	H
A-86	CH(CH ₃)C(CH ₃)=CH ₂	CH ₃
A-87	CH(CH ₃)C(CH ₃)=CH ₂	CH ₂ CH ₃
A-88	CH ₂ -C≡CH	H
A-89	CH ₂ -C≡CH	CH ₃
A-90	CH ₂ -C≡CH	CH ₂ CH ₃
A-91	cyclopentyl	H
A-92	cyclopentyl	CH ₃
A-93	cyclopentyl	CH ₂ CH ₃
A-94	cyclohexyl	H
A-95	cyclohexyl	CH ₃
A-96	cyclohexyl	CH ₂ CH ₃
A-97	CH ₂ -C ₆ H ₅	H
A-98	CH ₂ -C ₆ H ₅	CH ₃
A-99	CH ₂ -C ₆ H ₅	CH ₂ CH ₃

No.	R ¹	R ²
A-100	-(CH ₂) ₂ CH=CHCH ₂ -	
A-101	-(CH ₂) ₂ C(CH ₃)=CHCH ₂ -	
A-102	-CH(CH ₃)CH ₂ -CH=CHCH ₂ -	
A-103	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -	
A-104	-(CH ₂) ₃ CHFCH ₂ -	
A-105	-(CH ₂) ₂ CHF(CH ₂) ₂ -	
A-106	-CH ₂ CHF(CH ₂) ₃ -	
A-107	-(CH ₂) ₂ CH(CF ₃)(CH ₂) ₂ -	
A-108	-(CH ₂) ₂ O(CH ₂) ₂ -	
A-109	-(CH ₂) ₂ S(CH ₂) ₂ -	
A-110	-(CH ₂) ₅ -	
A-111	-(CH ₂) ₄ -	
A-112	-CH ₂ CH=CHCH ₂ -	
A-113	-CH(CH ₃)(CH ₂) ₃ -	
A-114	-CH ₂ CH(CH ₃)(CH ₂) ₂ -	
A-115	-CH(CH ₃)-(CH ₂) ₂ -CH(CH ₃)-	
A-116	-CH(CH ₃)-(CH ₂) ₄ -	
A-117	-CH ₂ -CH(CH ₃)-(CH ₂) ₃ -	
A-118	-(CH ₂)-CH(CH ₃)-CH ₂ -CH(CH ₃)-CH ₂ -	
A-119	-CH(CH ₂ CH ₃)-(CH ₂) ₄ -	
A-120	-(CH ₂) ₂ -CHOH-(CH ₂) ₂ -	
A-121	-(CH ₂) ₆ -	
A-122	-CH(CH ₃)-(CH ₂) ₅ -	
A-123	-(CH ₂) ₂ -N(CH ₃)-(CH ₂) ₂ -	
A-124	-N=CH-CH=CH-	
A-125	-N=C(CH ₃)-CH=C(CH ₃)-	
A-126	-N=C(CF ₃)-CH=C(CF ₃)-	

The compounds I are suitable as fungicides. They are distinguished by an outstanding effectiveness against a broad spectrum of phytopathogenic fungi, especially from the classes of the *Ascomycetes*, *Deuteromycetes*, *Oomycetes* and *Basidiomycetes*. Some are systemically effective and they can be used in plant protection as foliar and soil fungicides.

They are particularly important in the control of a multitude of fungi on various cultivated plants, such as wheat, rye, barley, oats, rice, maize, grass, bananas, cotton, soya, coffee, sugar cane, vines, fruits and ornamental plants, and vegetables, such as

cucumbers, beans, tomatoes, potatoes and cucurbits, and on the seeds of these plants.

They are especially suitable for controlling the following plant diseases:

- 5
 - *Alternaria* species on fruit and vegetables,
 - *Bipolaris* and *Drechslera* species on cereals, rice and lawns,
 - *Blumeria graminis* (powdery mildew) on cereals,
 - *Botrytis cinerea* (gray mold) on strawberries, vegetables, ornamental plants and grapevines,
- 10
 - *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* on cucurbits,
 - *Fusarium* and *Verticillium* species on various plants,
 - *Mycosphaerella* species on cereals, bananas and peanuts,
 - *Phytophthora infestans* on potatoes and tomatoes,
 - *Plasmopara viticola* on grapevines,
- 15
 - *Podosphaera leucotricha* on apples,
 - *Pseudocercospora herpotrichoides* on wheat and barley,
 - *Pseudoperonospora* species on hops and cucumbers,
 - *Puccinia* species on cereals,
 - *Pyricularia oryzae* on rice,
- 20
 - *Rhizoctonia* species on cotton, rice and lawns,
 - *Septoria tritici* and *Stagonospora nodorum* on wheat,
 - *Uncinula necator* on grapevines,
 - *Ustilago* species on cereals and sugar cane, and
 - *Venturia* species (scab) on apples and pears.

25

The compounds I are also suitable for controlling harmful fungi, such as *Paecilomyces variotii*, in the protection of materials (e.g. wood, paper, paint dispersions, fibers or fabrics) and in the protection of stored products.

- 30 The compounds I are employed by treating the fungi or the plants, seeds, materials or soil to be protected from fungal attack with a fungicidally effective amount of the active compounds. The application can be carried out both before and after the infection of the materials, plants or seeds by the fungi.
- 35 The fungicidal compositions generally comprise between 0.1 and 95%, preferably between 0.5 and 90%, by weight of active compound.

When employed in plant protection, the amounts applied are, depending on the kind of effect desired, between 0.01 and 2.0 kg of active compound per ha.

In seed treatment, amounts of active compound of 1 to 1000 g/100 kg of seed, preferably 1 to 200 g/100 kg, in particular 5 to 100 g/100 kg are generally used.

- 5 When used in the protection of materials or stored products, the amount of active compound applied depends on the kind of application area and on the effect desired. Amounts customarily applied in the protection of materials are, for example, 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of active compound per cubic meter of treated material.

10

The compounds I can be converted into the customary formulations, for example solutions, emulsions, suspensions, dusts, powders, pastes and granules. The application form depends on the particular purpose; in each case, it should ensure a fine and uniform distribution of the compound according to the invention.

15

The formulations are prepared in a known manner, for example by extending the active compound with solvents and/or carriers, if desired using emulsifiers and dispersants. Solvents/auxiliaries which are suitable are essentially:

- 20 - water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used,
- 25 - carriers such as ground natural minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example highly disperse silica, silicates); emulsifiers such as nonionic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignosulfite waste liquors and methylcellulose.

30

Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutyl naphthalenesulfonic acid, alkylaryl sulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore

35 condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ether, tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty

alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignosulfite waste liquors and methylcellulose.

- 5 Suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, 10 propanol, butanol, cyclohexanol, cyclohexanone, isophorone, strongly polar solvents, for example dimethyl sulfoxide, N-methylpyrrolidone and water.

Powders, materials for spreading and dustable products can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

- 15 Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active compounds to solid carriers. Examples of solid carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, 20 magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

- 25 In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active compound. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The following are examples of formulations: 1. Products for dilution with water

- 30 A Water-soluble concentrates (SL)
10 parts by weight of a compound according to the invention are dissolved in water or in a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active compound dissolves upon dilution with water.

35

B Dispersible concentrates (DC)

20 parts by weight of a compound according to the invention are dissolved in cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

5

C Emulsifiable concentrates (EC)

15 parts by weight of a compound according to the invention are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5%). Dilution with water gives an emulsion.

10

D Emulsions (EW, EO)

40 parts by weight of a compound according to the invention are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5%). This mixture is introduced into water by means of an emulsifying machine (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

15

E Suspensions (SC, OD)

In an agitated ball mill, 20 parts by weight of a compound according to the invention are comminuted with addition of dispersants, wetters and water or an organic solvent to give a fine active compound suspension. Dilution with water gives a stable suspension of the active compound.

20

F Water-dispersible granules and water-soluble granules (WG, SG)

50 parts by weight of a compound according to the invention are ground finely with addition of dispersants and wetters and made into water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound.

25

30

G Water-dispersible powders and water-soluble powders (WP, SP)

75 parts by weight of a compound according to the invention are ground in a rotor-stator mill with addition of dispersants, wetters and silica gel. Dilution with water gives a stable dispersion or solution of the active compound.

35

2. Products to be applied undiluted**H Dustable powders (DP)**

5 parts by weight of a compound according to the invention are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

40

I Granules (GR, FG, GG, MG)

0.5 part by weight of a compound according to the invention is ground finely and associated with 95.5% carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted.

J ULV solutions (UL)

10 10 parts by weight of a compound according to the invention are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended uses; the intention is to ensure in each case the finest possible distribution of the active compounds according to the invention.

20 Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

30 The active compound concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active compounds may also be used successfully in the ultra-low-volume process (ULV), by which it is possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

35 Various types of oils, wetters, adjuvants, herbicides, fungicides, other pesticides, or bactericides may be added to the active compounds, if appropriate not until immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.

The compositions according to the invention can, in the use form as fungicides, also be present together with other active compounds, e.g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers. Mixing the compounds I or the
 5 compositions comprising them in the application form as fungicides with other fungicides results in many cases in an expansion of the fungicidal spectrum of activity being obtained.

The following list of fungicides, in conjunction with which the compounds according to
 10 the invention can be used, is intended to illustrate the possible combinations but does not limit them:

- acylalanines, such as benalaxyl, metalaxyl, ofurace or oxadixyl,
- amine derivatives, such as aldimorph, dodine, dodemorph, fenpropimorph,
 15 fenpropidin, guazatine, iminoctadine, spiroxamine or tridemorph,
- anilinopyrimidines, such as pyrimethanil, mepanipyrin or cyprodinyl,
- antibiotics, such as cycloheximide, griseofulvin, kasugamycin, natamycin, polyoxin or streptomycin,
- azoles, such as bitertanol, bromoconazole, cyproconazole, difenoconazole,
 20 dinitroconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriatol, hexaconazole, imazalil, metconazole, myclobutanil, penconazole, propiconazole, flutriatol, zole, prochloraz, prothioconazole, tebuconazole, triadimefon, triadimenol, triflumizole or triticonazole,
- dicarboximides, such as iprodione, myclozolin, procymidone or vinclozolin,
- 25 • dithiocarbamates, such as ferbam, nabam, maneb, mancozeb, metam, metiram, propineb, polycarbamate, thiram, ziram or zineb,
- heterocyclic compounds, such as anilazine, benomyl, boscalid, carbendazim, carboxin, oxycarboxin, cyazofamid, dazomet, dithianon, famoxadone, fenamidone, fenarimol, fuberidazole, flutolanil, furametpyr, isoprothiolane, mepronil, nuarimol,
 30 probenazole, proquinazid, pyrifenoxy, pyroquilon, quinoxifen, silthiofam, thiabendazole, thifluzamide, thiophanate-methyl, tiadinil, tricyclazole or triforine,
- copper fungicides, such as Bordeaux mixture, copper acetate, copper oxychloride or basic copper sulfate,
- nitrophenyl derivatives, such as binapacryl, dinocap, dinobuton or nitrophthal-
 35 isopropyl,
- phenylpyrroles, such as fenpiclonil or fludioxonil,
- sulfur,
- other fungicides, such as acibenzolar-S-methyl, benthiavalicarb, carpropamid, chlorothalonil, cyflufenamid, cymoxanil, dazomet, diclomezine, diclocymet,

diethofencarb, edifenphos, ethaboxam, fenhexamid, fentin-acetate, fenoxanil, ferimzone, fluazinam, fosetyl, fosetyl-aluminum, iprovalicarb, hexachlorobenzene, metrafenone, pencycuron, propamocarb, phthalide, tolclofos-methyl, quintozone or zoxamide,

- 5 • strobilurins, such as azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin or trifloxystrobin,
- sulfenic acid derivatives, such as captafol, captan, dichlofluanid, folpet or tolylfluanid,
- 10 • cinnamides and analogous compounds, such as dimethomorph, flumetover or flumorph.

Synthesis examples

- 15 The procedures described in the synthesis examples below were used to prepare further compounds I by appropriate modification of the starting compounds. The compounds thus obtained are listed in the tables below, together with physical data.

Example 1: Preparation of diethyl 2-chloro-4-methoxyphenylmalonate

- 20 At about 60°C, diethyl malonate (0.49 mol) was added, over a period of 2 hours, to a suspension of sodium hydride (0.51 mol) in 140 ml of 1,4-dioxane. After a further 10 min of stirring, 0.05 mol of CuBr was added. After 15 min, 0.25 mol of 1-bromo-2-chloro-4-methoxybenzene in 10 ml of dioxane was added. The reaction mixture was kept at 100°C for about 14 hours, and 35 ml of 12N hydrochloric acid were
- 25 then added slowly at about 15°C. The precipitate was filtered off and the filtrate was extracted with diethyl ether. After phase separation, the organic phase was dried and then freed from the solvent. 34 g of the title compound remained.

Example 2: Preparation of

- 30 5,7-dihydroxy-6-(2-chloro-4-methoxyphenylphenyl)-[1,2,4]-triazolo[1,5-a]pyrimidine

- A mixture of 14 g of 3-amino-1,2,4-triazole, 0.17 mol of the ester from Example 1 and 50 ml of tributylamine (50 ml) was stirred at 180°C for about six hours. At about 70°C, a solution of 21 g of NaOH in 200 ml of water was added, and the mixture was stirred for
- 35 a further 30 min. The organic phase was separated off and the aqueous phase was extracted with diethyl ether. After acidification with conc. hydrochloric acid, the product precipitated from the aqueous phase. Filtration gave 32 g of the title compound.

Example 3: Preparation of

- 40 5,7-dichloro-6-(2-chloro-4-methoxyphenylphenyl)-[1,2,4]-triazolo[1,5-a]pyrimidine

5 A mixture of 30 g of the triazolopyrimidine from Example 2 and 50 ml of POCl₃ was heated under reflux for eight hours, and during this time, a little POCl₃ distilled off. The residue was added to a mixture of CH₂Cl₂ and water, the organic phase was separated off, washed and dried and the solvent was then removed. This gave 22 g of the title compound of m.p. 163°C.

Example 4: Preparation of 5-chloro-6-(2-chloro-4-methoxyphenyl)-7-but-2-ylamino-[1,2,4]-triazolo[1,5-a]pyrimidine [I-3]

10

A solution of 1.5 mmol of the 2-butylamine and 1.5 mmol of triethylamine in 10 ml of dichloromethane was added with stirring to a solution of 1.5 mmol of the product from Ex. 3 in 10 ml of dichloromethane. The reaction mixture was stirred at 20-25°C for about 16 hours and then washed with dil. hydrochloric acid. The organic phase was separated off and dried, and the solvent was removed. Chromatography on silica gel gave 250 mg of the title compound of m.p. 116°C.

15

Table I – Compounds of the formula I

No.	R ¹	R ²	L	R ³	X	phys. data (m.p. [°C])
	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	H	CH ₃	Cl	166
	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		H	CH ₃	Cl	203
	(±) CH(CH ₃)-CH ₂ CH ₃	H	H	CH ₃	Cl	116
	(R) CH(CH ₃)CH ₂ CH ₃	H	H	CH ₃	Cl	114
	(±) CH(CH ₃)-CH(CH ₃) ₂	H	H	CH ₃	Cl	139
	(R) CH(CH ₃)-CH(CH ₃) ₂	H	H	CH ₃	Cl	128
	(±) CH(CH ₃)-C(CH ₃) ₃	H	H	CH ₃	Cl	166
	(R) CH(CH ₃)-C(CH ₃) ₃	H	H	CH ₃	Cl	163
	(±) CH(CH ₃)-CF ₃	H	H	CH ₃	Cl	165
	(S) CH(CH ₃)-CF ₃	H	H	CH ₃	Cl	144
	CH ₂ CF ₃	H	H	CH ₃	Cl	186
	-CH ₂ CH(CH ₃)(CH ₂) ₂ -		H	CH ₃	Cl	138

Owing to the hindered rotation of the phenyl group, two diastereomers, which may have different physical properties, may exist.

Examples for the action against harmful fungi

The fungicide action of the compounds of the formula I was demonstrated by the following tests:

5

The active compounds were prepared as a stock solution comprising 0.25% by weight of active compound in acetone or DMSO. 1% by weight of the emulsifier Uniperol® EL (wetting agent having emulsifying and dispersing action based on ethoxylated alkylphenols) was added to this solution, and the mixture was diluted with water to the

10

Use Example 1 - Activity against early blight of tomato caused by *Alternaria solani*

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Leaves of potted plants of the cultivar "Goldene Prinzessin" were sprayed to runoff point with an aqueous suspension having the concentration of active compounds stated below. The next day, the leaves were infected with an aqueous zoospore suspension of *Alternaria solani* in 2 % biomalt solution having a density of 0.17×10^6 spores/ml. The plants were then placed in a water-vapor-saturated chamber at temperatures of between 20 and 22°C. After 5 days, the disease on the leaves of the untreated, but infected control

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plants had developed to such an extent that the infection could be determined visually in %.

In this test, the plants which had been treated with 63 ppm of the compounds I-1, I-3, I-10 or I-12 showed no infection, whereas the untreated plants were 90% infected.

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Use Example 2 - Activity against gray mold on bell pepper leaves caused by *Botrytis cinerea*

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Bell pepper seedlings of the cultivar "Neusiedler Ideal Elite" were, after 4-5 leaves were well developed, sprayed to runoff point with an aqueous suspension having the concentration of active compound stated below. The next day, the treated plants were inoculated with a spore suspension of *Botrytis cinerea* which contained 1.7×10^6 spores/ml in a 2% strength aqueous biomalt solution. The test plants were then placed in a climatized chamber at 22-24°C and high atmospheric humidity. After 5 days, the

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extent of the fungal infection on the leaves could be determined visually in %.

In this test, the plants which had been treated with 63 ppm of the compound I-12 showed no infection, whereas the untreated plants were 90% infected.